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Alkoxyalumoxanes

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The reaction of aluminum alkoxide or aluminum metal in primary alcohols at 250−300 °C was examined, and the products were characterized by powder X-ray diffraction, IR spectroscopy, MAS NMR spectroscopy, thermal analyses, and scanning electron microscopy. The products had the layer structure of boehmite with alkyl pendant groups derived from the solvent alcohols, the alkyl moieties of the aluminum alkoxide being completely expelled from the product, and the basal spacing linearly increased with the carbon number of the alcohol. The alkyl groups were stable beyond the boiling point of the parent alcohol, suggesting that they are covalently bonded to the boehmite layers. All of the data suggest that the products are the alkyl derivatives of boehmite (alkoxyalumoxanes) having an empirical formula of $AlO(OH)_{(1-x)}(OR)_x$. The value x depended on the alcohol used as the solvent and varied from 0.62 to 0.21. Partial decomposition of alkyl moieties still preserved the overall structure of alkoxyalumoxane.

Introduction

Methylalumoxane is formed by partial hydrolysis of trimethylaluminum and was found to be a good cocatalyst for the Kaminsky-type polymerization catalysts.[1,2] However, the structure of the methylalumoxane is not yet fully understood. Recently, Barron and co-workers carried out the structural investigation of the some of the related compounds and concluded that they have the boehmite core structure.[3,4] They also reported the synthesis of carboxylatoalumoxanes by the reaction of boehmite with carboxylic acids.[5]

Boehmite is one of the modifications of aluminum oxide hydroxide, AlOOH.[6] Although boehmite has a structure closely related to that of FeOCl, which readily forms intercalation compounds,[7] direct intercalation of guest molecules into boehmite layers has never been reported, presumably because of strong hydrogen bonding between the layers.

On the other hand, in the pioneering work by Kubo and Uchida,[8] it was reported that the reaction of gibbsite with methanol yielded the methyl derivative of boehmite ($AlO(OH)_{0.5}(OCH_3)_{0.5}$). Inoue et al. reported that the reaction of gibbsite in glycols such as ethylene glycol and 1,4-butanediol yielded glycol (i.e., ω-hydroxyalkyl) derivatives of boehmite.[9−12] These compounds have the layer structure of boehmite, and a part of protons of the surface hydroxyl groups are substituted with the methyl or ω-hydroxylalkyl groups. Therefore, these compounds can be regarded as alkoxyalumoxanes.

Kubo and Uchida[8] concluded that their reaction proceeded by means of a solid-state reaction that proceeded by the diffusion of methanol molecules in the solid gibbsite lattice with the aid of the Hedvall effect.[13] Inoue et al. reported that the reaction of gibbsite in ethanol or higher alcohols did not yield the alkyl derivatives of boehmite (i.e., alkoxyalumoxanes) but afforded well-crystallized boehmite together with χ-alumina, which was formed by thermal decomposition of gibbsite.[14,15] They concluded that the difficulty in the formation of the alkyl derivatives of boehmite by the solid-state reaction is due to the difficulty in the diffusion of molecules larger than methanol into the gibbsite lattice.[12]

Inoue et al. concluded that the reaction of gibbsite in glycols proceeded by a dissolution−crystallization mechanism, because the morphology of the product was completely different from that of the starting material.[9,12] They found that a hydroxyl group and another functional group such as hydroxyl, amino, or methoxyl group having the ability to donate its lone pair electrons were necessary for the organic solvent molecules to form the boehmite derivatives by this mechanism.[12] In this regard, Laine et al. recently reported that the reaction

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of aluminum hydroxide in triethanolamine at 200 °C yielded a mononuclear triethanolamine−aluminum complex, $N(CH_2CH_2O)_3Al$.[16]

Inoue et al.[17,18] also examined the reaction of aluminum alkoxides in various glycols and found that the reaction yielded the glycol derivative of boehmite, the same compound that was obtained by the reaction of gibbsite. However, synthesis of the simple alkyl derivatives of boehmite (alkoxyalumoxanes) other than the methyl derivative has not been reported until our recent brief report that the reaction of aluminum metal in alcohols directly yielded the alkyl derivatives of boehmite.[19] As the reaction was believed to proceed via aluminum alkoxide, we also examined the reaction of aluminum alkoxides in alcohols at high temperatures, and these results will be reported here in detail.

Experimental Section

Synthesis Methods. In a Pyrex test tube serving as autoclave liner, 85 mL of an alcohol and 0.6 g (22 mmol) of aluminum foil were placed, and the test tube was then placed in a 200 mL autoclave. In the gap between the autoclave wall and the test tube was placed an additional 20 mL of the alcohol. The autoclave was thoroughly purged with nitrogen, heated to the desired temperature (250−300 °C) at a rate of 2.5 °C min^{-1}, and held at that temperature for 2 h. After the assembly was cooled to room temperature, the resulting precipitates were washed by repeated cycles of agitation with methanol, centrifuging, and decantation and then air-dried.

For the reaction of aluminum alkoxides, commercially available aluminum isopropoxide (Nacalai Tesuque), aluminum ethoxide (Aldrich), and aluminum *n*-butoxide (Wako) were used without further purification. Note, however, a small-quantity bottle was purchased, and a bottle of reagent was used in a couple of days, discarding the remaining alkoxide. Aluminum alkoxide (22.7 mmol) was allowed to react in alcohols according to the same procedure as mentioned above.

The aluminum-based yields of the products of these two types of the reaction calculated by ignition loss were 80−100%. Small loss was due to overflow of the reaction mixture from the test tube.

Characterization. Powder X-ray diffraction (XRD) was measured on a Shimadzu XD-D1 diffractometer using Cu Kα radiation and a carbon monochromator. Infrared (IR) spectra were obtained on a Shimadzu IR-435 spectrometer with the usual KBr-pellet technique. The NMR spectra were obtained on a JEOL GSX-270 spectrometer equipped with a Doty ultrasonic sample spinning probe. About 10 kHz sample spinning at the magic angle was used. The ^{27}Al NMR spectra were recorded at 70.3 MHz, and the ^{13}C NMR spectra were recorded at 37.8 MHz using the cross-polarization (CP) technique. Simultaneous thermogravimetric (TG) and differential thermal analyses (DTA) were performed on a Shimadzu DTG-50 analyzer: A weighed amount (ca. 30 mg) of the sample was placed in the analyzer, dried in a 40 mL min^{-1} dried air flow until no more weight decrease was observed, and then heated at the rate of 10 °C min^{-1} in the same gas flow. TG-mass (MS) spectra were recorded on a Shimadzu QP-1000 mass spectrometer equipped with a Shimadzu TG-50 thermobalance. Helium gas was made to flow through the thermobalance, the effluent gas was introduced to the mass spectrometer via a separator, and molecules were ionized by electron impact with 70 eV. Morphologies of the products were observed with a scanning electron microscope (SEM), Hitachi S-2500CX. Elemental analyses for C and H were performed at the Laboratory of Organic Elemental Microanalysis, Kyoto University, Japan. For NMR, IR, and elemental analyses, the samples were dried beforehand over P_2O_5 in vacuo at 100 °C for 2 h.

Results

The reaction of aluminum metal in ethanol or 1-butanol at 250 °C for 2 h yielded crystalline products, but amorphous products were obtained in the other lower alcohols. When the reaction was carried out at 300 °C, the straight-chain primary alcohols with the carbon number 10 or less gave the crystalline products, which will be shown to be the alkyl derivatives of boehmite (alkoxyalumoxanes). A low-molecular-weight branched alcohol, 3-methyl-1-butanol, gave an amorphous product, when the reaction was quenched at 2 h, but prolonged reaction (8 h) gave the alkyl derivative of boehmite. The reactions in straight-chain primary alcohols with the carbon number larger than 10 and in 2-ethyl-1-hexanol resulted in recovery of aluminum metal, even with prolonged reaction time.

The reaction of aluminum isopropoxide in place of aluminum metal in the straight-chain primary alcohols also gave the alkyl derivatives of boehmite. In this reaction, 1-dodecanol and 3-methyl-1-butanol also gave the boehmite derivatives, which shows a sharp contrast against the results for the reaction of aluminum metal. On the other hand, the reaction of aluminum isopropoxide in 2-ethyl-1-hexanol, 2-methyl-1-butanol, and the straight-chain primary alcohols with the carbon number larger than 16 yielded amorphous products. Whereas the last solvents yielded amorphous products even with the prolonged reaction time, prolonged reaction time (8 h) in the former two solvents resulted in formation of χ-alumina, which was also obtained by the reaction of aluminum alkoxides in inert organic solvents such as toluene.[20] The reaction of aluminum isopropoxide in 2-methoxyethanol and 2-aminoethanol did not yield any solid products, and homogeneous solutions were obtained after the reaction. These results together with literature results[8−12,14,15,17,18,20−22] are summarized in Table 1.

The XRD patterns of the products obtained by the reaction of aluminum metal and aluminum isopropoxide were essentially identical to each other, and they are shown in Figure 1. For comparison, the XRD pattern of pseudoboehmite (microcrystalline boehmite) is also shown in the figure. The XRD patterns of the products resembled those of pseudoboehmite and the glycol derivatives of boehmite and could be indexed on the basis of the boehmite structure, suggesting that the present products had a structure similar to that of the glycol derivative of boehmite. The lattice parameters *a* and *c* of the products are essentially identical with those of well-crystallized boehmite. However, the interlayer spacings of the products were much longer than that of boehmite and increased with the increase in the carbon number of the alcohol used as the solvent (Figure 2), suggesting that the alkyl groups derived from the

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Table 1. Reaction of Aluminum Source in Organic Solvent at High Temperatures

		reaction			
Al source[a]	solvent[b]	temp. (°C)	time (h)	product[c]	ref
metal	*n*-ROH (C1−C10)	300	2	BD	this work
metal	*n*-ROH ($C > 10$)	300	8	no reaction	this work
metal	2-alkyl-1-alkanol[d]	300	8	no reaction	this work
metal	3-methyl-1-butanol	300	8	BD	this work
metal	glycols	300	2	no reaction	this work
AIP	*n*-ROH (C1−C12)	300	2	BD	this work
AIP	3-methyl-1-butanol	300	2	BD	this work
AIP	*n*-ROH ($C > 16$),	300	8	amorphous	this work
AIP	2-alkyl-1-alkanol	300	8	χ-alumina	this work
AIP	glycols	300	2	BD	17,18
AIP	MOE, AE	300	2	homogeneous solution	this work
AIP	inert organic solvent	300	2	χ-alumina	20
AIP	none	420		amorphous alumina	21
ASB	2-butanol	250	6.5	χ-alumina, boehmite	22
gibbsite	methanol	180−260	1	BD	8
gibbsite	*n*-ROH (C1−C4)	250	2	boehmite	14,15
gibbsite	*n*-ROH ($C > 5$)	250	2	boehmite, χ-alumina	14,15
gibbsite	Glycols	250	2	BD	9−12
gibbsite	MOE, AM	250	2	BD + unreacted gibbsite	11
gibbsite	triethanolamine	200	1−2	complex	16
gibbsite	inert organic solvent	250	2	boehmite	11

[a] AIP, aluminum isopropoxide; ASB, aluminum *sec*-butoxide. [b] *n*-ROH, straight-chain primary alcohol; MOE, 2-methoxyethanol; AE, 2-aminoethanol. [c] BD, the boehmite derivative. [d] 2-Methyl-1-butanol and 2-ethyl-1-hexanol were examined.

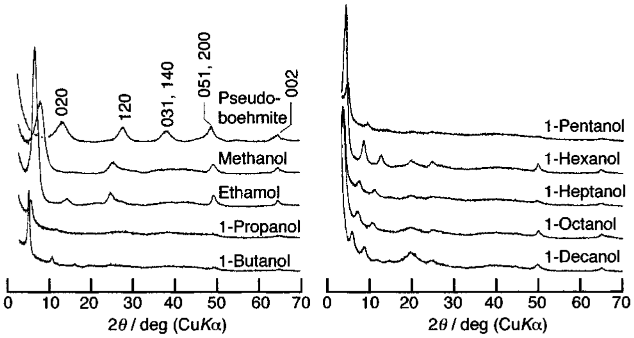

Figure 1. XRD patterns of pseudoboehmite and the products obtained by the reaction of aluminum metal or aluminum isopropoxide in the alcohols specified in the figure.

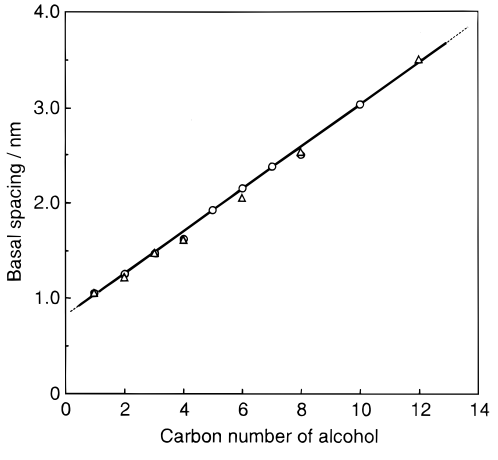

Figure 2. Interlayer spacings of the products obtained by the reaction of: ○, aluminum metal; △, aluminum isopropoxide; in straight-chain primary alcohols. The slope of the plot had a value of 2.21 Å/CH$_2$.

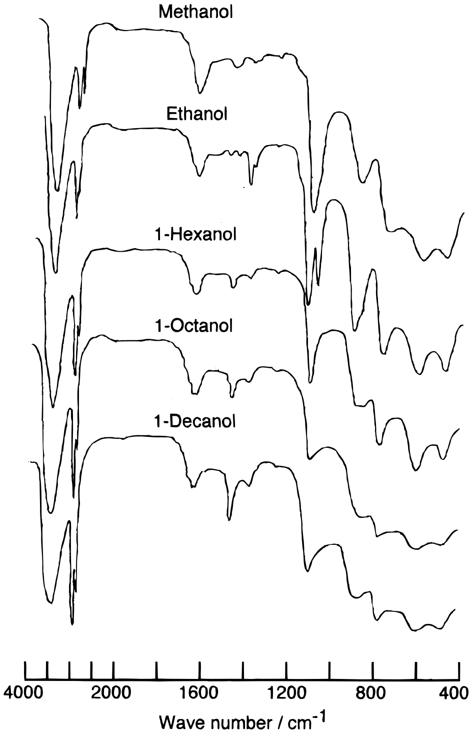

Figure 3. IR spectra of the products obtained by the reaction of aluminum isopropoxide or aluminum metal in the alcohols specified in the figure.

solvent alcohols are incorporated between the boehmite layers. From Figure 2, the slope was calculated to be 2.21 Å/CH$_2$.

The IR spectra of the products are given in Figure 3. The products exhibited the bands due to the alkyl groups at essentially identical positions as those observed for liquid alcohols. Note that the products obtained by the reactions of aluminum metal and aluminum isopropoxide exhibited essentially identical spectra and that there is no indication of the presence of the isopropoxyl group in the products obtained from aluminum isopropoxide. Bands due to the boehmite structure were seen at 773, 615, and 478 cm^{-1},[23,24] but

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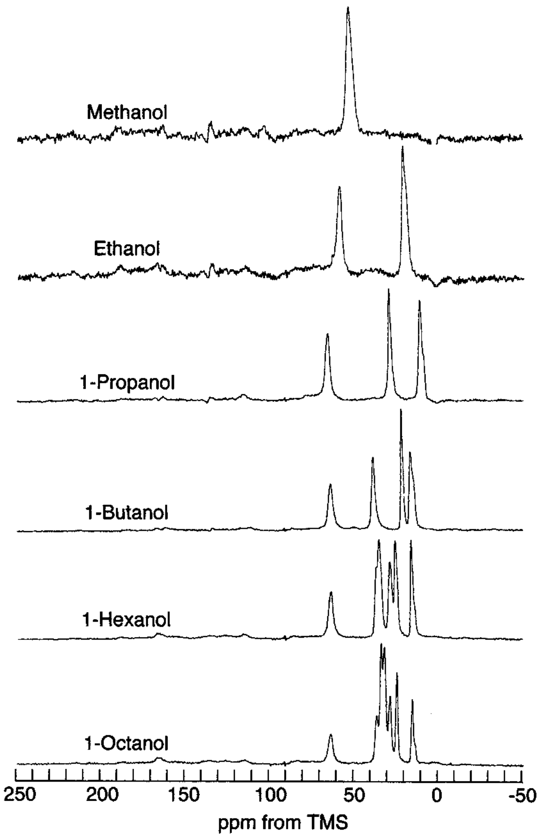

Figure 4. CP MAS ^{13}C NMR spectra of the products obtained by the reaction of aluminum isopropoxide in the alcohols specified in the figure.

bands characteristic of the hydrogen bonding between two adjacent boehmite layers were not observed, suggesting that the boehmite layers are separated by incorporation of the alkyl groups between the boehmite layers.

The cross-polarization magic-angle spinning (CP MAS) ^{13}C NMR spectra of the products are shown in Figure 4. All of the spectra of the products exhibited a peak at around 60 ppm due to the methylene carbon at the α position to the oxygen. Methyl and methylene carbons were observed at the positions essentially identical to those observed for the parent alcohol, which is due to the fact that the anisotropic effect caused by substitution of the OH group by the OAl< group is relatively small.[18,25] Again, the isopropyl group was not detected although aluminum isopropoxide was used as the starting material. The peak due to α-methylene was broader than the other peaks, suggesting that the alkyl moieties are rigidly bound to the boehmite layers through the oxygen atom whereas other carbons, especially those in the long carbon chain, had much more freedom.

The MAS ^{27}Al NMR spectra of the products (data not shown) indicated that the Al atoms in the products obtained in the lower alcohols were solely octahedrally coordinated whereas the products from higher alcohols contained a small amount of tetrahedrally coordinated aluminum atoms.

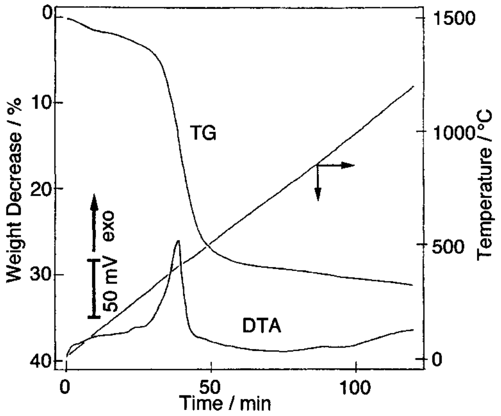

Figure 5. Thermal analysis of the product obtained by the reaction of aluminum metal in ethanol at 250 °C, in a 40 mL min^{-1} flow of dried air at the heating rate of 10 °C min^{-1}.

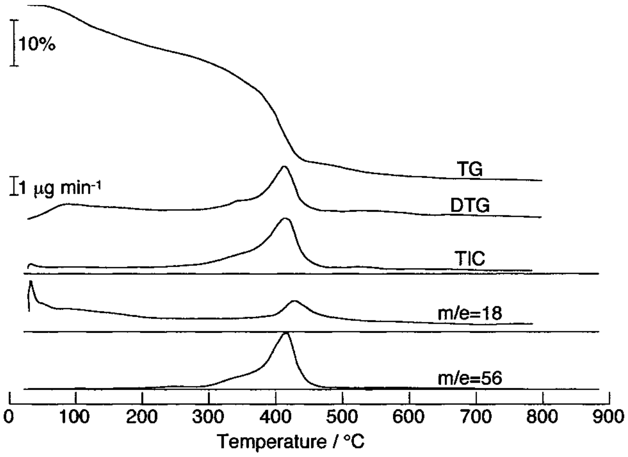

Figure 6. Thermogravimetric analysis of the product obtained by the reaction of aluminum isopropoxide in 1-butanol at 250 °C and ion chromatography of the effluent gas. Flow gas, 30 mL min^{-1} of helium; heating rate of 5 °C min^{-1}.

Figure 5 shows the result of thermal analyses of the product obtained by the reaction of aluminum metal in ethanol as a representative result. Thermogravimetric trace showed a sharp weight decrease at around 400 °C, which was associated with a large exothermic response in DTA, suggesting that the weight decrease is due to combustion of the organic moieties incorporated between the boehmite layers. XRD analysis of the samples heated at various temperatures showed that the layer structure was maintained until this weight decrease, although the interlayer spacing was slightly decreased and the diffraction peak was broadened (data not shown). Because the layer structure remained beyond the boiling point of the alcohol, one can conclude that the alkyl moieties are bound to the boehmite layers through covalent bonds. To examine the origin of the weight decrease, TG-MS experiments were carried out. As shown in Figure 6, the weight decrease took place in wider temperature range and at slightly higher temperature as compared with the result shown in Figure 5, which can be attributed to the difference in the experimental conditions (flow gas and heating rate). Fragment ions due to olefins were detected over the temperature range of the weight decrease, and at the latter part of the weight decrease (400−510 °C), water ($m/e = 18$) was removed. It is known that, on calcination, well-crystallized boehmite decomposes into γ-alumina

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Table 2. Elemental Analyses[a]

	found			calcd for $AlO(OH)_{(1-x)}(OR)_x$			
alcohol	C (%)	H (%)	ignition loss (%)	x	C (%)	H (%)	ignition loss (%)
methanol	10.1	3.6	25.5	0.62	10.8	3.3	25.7
ethanol	13.1	3.7	27.7	0.39	13.2	3.6	28.1
1-propanol	10.2	3.8	23.7	0.22	11.4	3.4	26.4
1-butanol	13.1	3.6	28.0	0.23	14.9	3.9	29.8
1-hexanol	21.6	5.2	38.0	0.25	22.2	5.0	37.1
1-octanol	21.8	5.4	38.6	0.21	23.7	5.2	38.6
1-decanol	31.2	6.8	49.3	0.28	33.5	6.6	48.3

[a] Samples were dried in vacuo at 100 °C for 2 h.

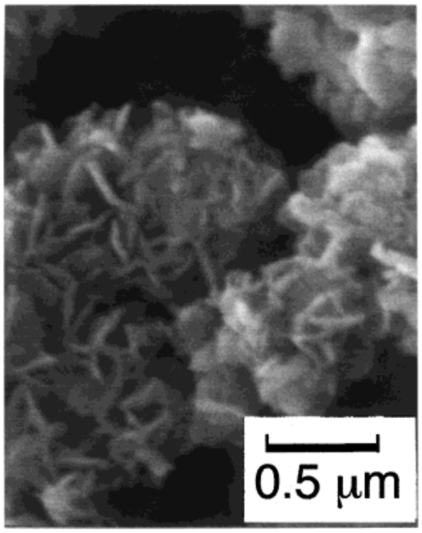

Figure 7. Scanning electron micrograph of the product obtained by the reaction of aluminum metal in ethanol at 250 °C for 2 h.

at around 550 °C and that with decreasing crystallite size of boehmite the decomposition takes place at lower temperatures.[26,27] Therefore, the latter process is due to the decomposition of boehmite layers yielding γ-alumina and water, which occurred after the decomposition of alkyl groups of the alkyl derivative of boehmite.

Analytical results and ignition losses determined by TG analysis for the products are summarized in Table 2. From the results, empirical formulas, $AlO(OH)_{(1-x)}(OR)_x$, of the products are calculated, and the results are also shown in Table 2.

A scanning electron micrograph (SEM) of the product is shown in Figure 7. The alkyl derivatives of boehmite had a honeycomb-like texture formed by random orientation of wrinkled sheets of the boehmite layers, which can be formed by stacking defects, as was originally proposed by Pierre and Uhlmann[28] to explain the morphology of a pseudoboehmite sample, similar to that observed in the present products. Similar morphology was also observed for the glycol derivative of boehmite.[10-12,18]

The reactions of aluminum ethoxide and n-butoxide gave the products having alkyl moieties derived from the solvent alcohols (data not shown).

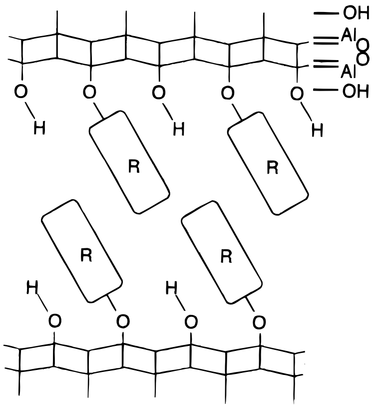

Figure 8. Proposed structure of the products (alkoxylalumoxanes).

When a small amount of water was intentionally added to the solvent alcohol, the reaction of aluminum alkoxide resulted in formation of pseudoboehmite, whereas the reaction of aluminum metal resulted in recovery of the starting material.

Discussion

All of the experimental results suggested that the products were alkyl derivatives of boehmite (alkoxyalumoxane) having a structure as depicted in Figure 8.

It is well-known that aluminum alkoxides are easily hydrolyzed by the moisture.[29,30] Nevertheless, the present products are stable to moisture and can be handled in the ambient atmosphere, although they have the Al—O—C bonds. Similar interlamellar alkyl derivatives of kaolinite having the Al—O—C bonds were recently reported by Tunney and Detellier.[31,32] Because hydrolysis of Al—O—C bonds is initiated by nucleophilic attack of water at aluminum atom,[29,30] tetrahedrally coordinated aluminum atoms would be easily subjected to the attack. On the other hand, the aluminum atoms in the present products are in the boehmite layer structure and are rigidly surrounded by six oxygen atoms. Therefore, nucleophilic attack of water toward the aluminum atoms is difficult so that the present products were stable to the moisture.

For the ordinary intercalation compounds, for example, for a zirconium phosphate-alkylamine system,[33] population of guest molecules in the inorganic layer is determined by the charge or proton density in the host layers and therefore remains at constant value with the variation of the alkyl chain of the guest molecules. On the other hand, in the present system, any ratio of alkyl substituent is allowed, and decomposition of a part of alkyl groups into olefin molecules leaving hydroxyl groups on the boehmite layer does not alter the overall structure of the alkyl derivative of boehmite. The only effect is the slight decrease in the interlayer spacing. This behavior is not specific for the alkyl derivatives of boehmite but is, we believe, one of general characteristics of organic derivatives of layered inorganics.

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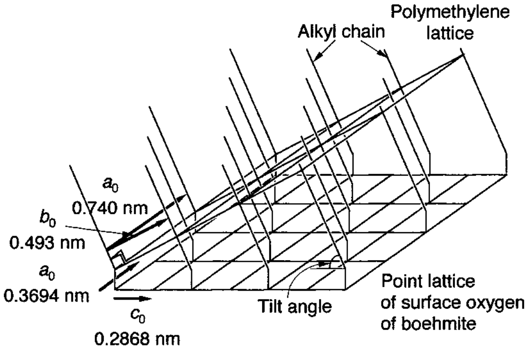


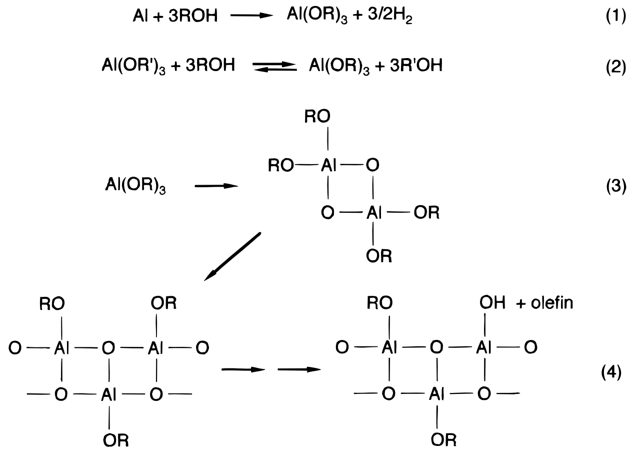
Figure 9. Proposed ideal alignment of alkyl chains on the boehmite lattice.

As shown in Figure 2, the steady increase in interlayer spacing with a slope of 2.21 Å/CH_2 was observed. When one assumes that the alkyl moieties form a bilayer of fully extended (i.e., all-trans) alkyl chains, the tilt angle of the alkyl chain with respect to the boehmite layer can be calculated to be 60.5° on the basis of typical methylene repeated distance of 1.27 Å/CH_2 for an all-trans polymethylene.[34]

Because the a_0 parameter (0.740 nm) of the crystalline polymethylene lattice[35] is approximately twice as large as the a_0 parameter (0.3694 nm)[36] of the boehmite lattice, the ideal alignment of alkyl moieties on the boehmite lattice is supposed to be as is depicted in Figure 9. Because two times the value of c_0 (0.2868 nm) of boehmite was larger than b_0 (0.493 nm) of the polymethylene lattice, alkyl chain should be tilted toward the c direction of the boehmite lattice to maximize the Coulomb interaction between the alkyl chains. The tilt angle can be calculated by the relation between these two parameters as $\sin^{-1}$ (0.493/(0.2868 × 2)) yielding 59.2°, which is in good agreement with the value calculated from the basal spacing versus carbon number plot. Therefore, we concluded the ideal alignment of the alkyl moiety is as depicted in Figure 9. Owing to the aligned alkyl pillars, the basal peaks of the alkoxyalumoxanes with longer carbon chain seems to be sharp. However, this alignment requires the alkyl/aluminum ratio of 0.5, which was much larger than that observed for the alkoxyalumoxanes with longer carbon chains. Random elimination of alkyl chains from the ideal alignment would produce the distribution of location of alkyl chains, and the basal spacing would be determined by the tilt angle of the alkyl chains where they are most crowded. Actually, partial decomposition of decoxyalumoxane (20% of decyl group was decomposed by heating at 340 °C) caused only small shrinkage of the basal spacing from 3.034 to 2.94 nm. Therefore, distribution of alkyl chains on the boehmite layer may not be homogeneous, but crowded alkyl chains would aligned as depicted in Figure 9, which determine the basal spacings of the alkoxyalumoxanes.

The formation of a alkyl derivative of boehmite from Al metal and aluminum alkoxide seems to involve several primary reactions, as depicted in Scheme 1.

Scheme 1. Reaction Mechanisms



Reaction 1 is the oxidation of aluminum metal with alcohol, yielding aluminum alkoxide and hydrogen. This reaction is irreversible and has a large driving force. Reaction 2 is the alcoholysis of $Al(OR)_3$ by the solvent alcohol, forming another aluminum alkoxide as an intermediate. Reaction 3 is the formation of a primary framework of boehmite, and reaction 4 is the growth of the boehmite layer.

Because the reaction temperature, 300 °C, was higher than the critical points of lower alcohols (methanol, 239 °C; ethanol, 239 °C; 1-propanol, 264 °C; 1-butanol, 289 °C; 2-propanol, 235 °C),[37] lower alcohols were in the supercritical condition. Reaction 2 is reversible and therefore the equilibrium composition of reaction 2 is determined by the fugacities of the two alcohols. The total amount of the alcohol charged in the autoclave was 2.59 mol for methanol, and the theoretical amount of 2-propanol liberated from $Al(OPr^i)_3$ was 0.068 mol; therefore, a much larger amount of the solvent alcohol was present in the system. With the increase in carbon number of the solvent alcohol, the number of moles of the charged alcohol was decreased. However, the boiling point of the alcohol increases with the carbon number, and most of the 2-propanol derived from the alkoxide escaped from the condensed phase into the gas phase. Moreover, because 2-propanol has a secondary hydroxyl group, it is easily dehydrated, yielding propylene and water. Therefore, reaction 2 would proceed completely to the intermediate, and as a result, the isopropyl (or isopropoxyl) groups derived from the alkoxide were completely expelled from the product.

The present products had empirical formulas of $Al(OH)_{(1-x)}(OR)_x$ (x = 0.62−0.21), which means more than two of the three R−O−Al< bonds must be broken at either the C−O or Al−O bond. The cleavage of the Al−O bond to produce an alkoxide anion can proceed via hydrolysis. Although the present reaction was carried out without addition of water, a small amount of water may be present in the alcohol sample and is possibly formed by the thermal decomposition of the alcohol. However, the addition of water to the reaction of aluminum alkoxide resulted in formation of pseudoboehmite, which is the product of direct hydrolysis of

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the aluminum alkoxide.[38] Because alcoholysis of aluminum isopropoxide (reaction 2) forms 2-propanol, this alcohol would decompose, yielding propylene and water, which may partly hydrolyze the intermediate and facilitate the development of the crystal structure of the product. However, this idea is not the sole route for the cleavage of the R−O−Al bonds because aluminum ethoxide and *n*-butoxide also yielded the same product. Therefore, cleavage of the C−O bond seems to take place. In previous papers,[20,39−41] we examined the reaction of metal alkoxide in inert organic solvents and found that the rate of the decomposition of alkoxide is determined by the structure of the alkyl group: *tert*-Alkoxides decomposed at lower temperatures, yielding amorphous products, and secondary alkoxides decomposed at 250−300 °C, yielding crystalline products, whereas primary alkoxides did not decompose at 300 °C. These results suggest that the decomposition of metal alkoxides is determined by the heterolytic cleavage of the C−O bond of metal alkoxides. This idea can be applied also to the present case, and heterolytic cleavage of the C−O bond took place for the development of the crystal structure. The difference in the reactivity of primary alkoxides in inert organic solvents and in alcohols can be attributed to the polarity of the solvent. Because alcohols are much more polar than inert organic solvents such as toluene, heterolytic cleavage of the C−O bonds of the intermediate proceeds more easily in alcohols than in inert organic solvents.

When the reactions of aluminum metal and aluminum alkoxides are compared, the reaction of aluminum alkoxides proceeded for a wider scope of alcohols. For example, aluminum metal did not react with 1-dodecanol and 2-methyl-1-butanol at 300 °C for 2 h, whereas aluminum alkoxides reacted with these solvents, yielding the alkyl derivatives of boehmite. This result indicates that polarity and steric bulkiness around the hydroxyl group of the alcohol are important for the reaction of aluminum metal with alcohol.

Addition of a small amount water to the alcoholic media also gives completely different effects for the reactions of aluminum metal as compared to those for the aluminum alkoxides. Whereas aluminum alkoxides yielded pseudoboehmite, the reaction of aluminum metal resulted in the recovery of aluminum metal. Because water is much reactive than alcohols, boehmite superficial layer was formed by the reaction of aluminum metal, which prevented the reaction of aluminum metal with alcohols.

Hydrothermal oxidation of metals have been examined for the synthesis of oxides. Thus, Torker et al.[42,43] examined the reaction of aluminum metal in water in the temperature range of 200−500 °C and found that various phases such as KI form (Tohdite) and α*-alumina were formed, depending on the reaction conditions. On the other hand, the use of alcohols in place of water for the hydrothermal oxidation of metals have never been examined from the viewpoint of inorganic synthesis although the reaction has been examined from the viewpoint of metal corrosion in alcohols.[44] The present paper demonstrated that the oxidation of metals in alcohols is a new route for the synthesis of inorganic materials.

In summary, the reaction of aluminum metal or aluminum alkoxides in alcohols at 250−300 °C yields alkoxyalumoxanes (alkyl derivatives of boehmite), in which alkyl groups are covalently bonded to the boehmite layers. Formation of aluminum alkoxides derived from the solvent alcohol by the reaction of aluminum metal with the alcohol or alcoholysis of metal alkoxide with the solvent alcohol is the first step of the reaction, and thermal decomposition of the aluminum alkoxides yields alkoxyalumoxanes.

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